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MATERIALS SELECTION AND PERFORMANCE CRITERIA FOR HYDROGEN PIPELINE TRANSMISSION

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ABSTRACT

As a part of worldwide Hydrogen Fuel Initiatives, hydrogen fuel cell technology (US DOE 2003) is being championed as a viable resource while at the same time recognizing that the production, transmission and end use distribution of hydrogen gas will be the most critical elements. The application of fuel cell technology when fully developed is expected to dominate power and auto industries worldwide. As the demand for hydrogen increases, issues related to the safe design and economic construction of hydrogen supply and transportation infrastructure will emerge as critical path items requiring serious consideration. One of the barriers for viable hydrogen economy is that the current guidelines in various codes and standards and regulations are not adequate for the required service conditions for hydrogen transportation and delivery Thus is the requirement for Multi-Year Research, Development and Demonstration Plan (MYPP) for the development of codes and standards to support hydrogen economy, (US DOE , 2002 & 2003).

The purpose of this paper is to identify current materials used in hydrogen service, their applicability and limitations, and to develop materials selection and performance criteria for designing safe hydrogen pipeline transmission infrastructure to support the development of hydrogen codes and standards, initiated by ASME (2003). Additionally, some critical materials research areas are recognized for future research.

Although for many decades within the chemical industry, hydrogen in various forms has been transported by various modes, including pipelines, tank cars, mobile re-chargers etc., the service conditions and transport requirements are significantly different when developing more economical methods for large volume hydrogen transportation. As industry moves quickly to implement an economical and effective pipeline infrastructure, either with new construction or by converting existing pipeline, understanding of material selection and performance, joining/welding, and establishing consensus for codes and standards are critical. Additionally, government regulations must be developed to ensure acceptable safety levels and public acceptance.

Pipeline transportation of hydrogen dates back to late 1930's. Current world experience is of the order of 3000 kilometers (1900 miles) of hydrogen transmission pipelines up to 14" diameter, mostly designed to transport hydrogen in-plant for commercial use for feedstock or for pipeline fuel. In USA there is 1300 Kilometers (800 miles of pipeline) infrastructure, predominantly owned by Air Products, Praxair, Air Liquide and El Paso. Materials of construction range from different varieties of stainless steel, high and low grades of carbon steel, ductile cast iron and various alloys of aluminum alloys, copper, nickel and titanium. Polymer/fiber glass reinforced pipes are also used, as in-plant piping at moderate temperatures. These pipelines generally operated at less than 1000 PSI, with a good safety record.

Essentially, hydrogen is obtained by synthesizing hydrogen containing compounds, such as natural gas, and other fossil fuels, and water and is stable in gaseous state at ambient temperatures. Hydrogen can be cooled and pressurized at cryogenic temperatures to a liquid or solid state. It is the lightest and the most abundant element in the universe. Its density 0.09 Kg/M^3 (at 0^o C and 101.325 kPa) makes it one of the most difficult gases to store and transport in large quantities. Hydrogen reacts with many types of pipeline metals, especially at higher pressures. This reaction is more specific to higher strength steels, whether it is "hydrogen induced cracking" (HIC), "hydrogen corrosion cracking" (HCC), or "hydrogen embrittlement" (HE). Many other materials suitability issues remain unanswered due to limited understanding or limited quantitative assessment for hydrogen compatibility. These issues include loss of material strength, fracture toughness, enhanced fatigue crack growth rates, low cycle fatigue, sub-critical & sustained load cracking, susceptibility to stress corrosion cracking, and hydrogen induced cracking in welds and joints. In particular, this paper will give attention to higher strength pipeline steels (i.e. API 5LX Grade 65 and higher), quenched and tempered steels, stainless steels, as well as those alloy steels used for pressure vessels and piping. Recent development of composite reinforced line pipe (CRLP™) has the potential as viable alternative to use of very high strength thermo-mechanically treated line pipe steels, but many issues related design parameters, construction and maintenance require research and development efforts.

INTRODUCTION/BACKGROUND

Hydrogen is the most abundant of all elements in the universe and it is thought the heavier elements were, and still are, being built from hydrogen and helium. In 1783 it was named hydrogène by Antoine Lavoisier, because when hydrogen burns, water is produced. Thus the name hydrogen is derived from Greek combination of words: **ὕδωρ (hydōr) = water + γεινομαι (geinomai) = to engender, bringing forth water** (Van der Krog, 2003).

Hydrogen makes up more than 90% of all atoms or three quarter of the mass or the universe. It is present as a free element in the atmosphere, but only to the extent of less than 1 ppm by volume. It is lightest of all gases and combines with other elements, sometimes explosively to form compounds.

Hydrogen gas in its purest condition is clear and odorless and burns in air or oxygen atmosphere with a transparent flame. The flammability range is wide 4 -75 percent in air with an ignition energy as low as 0.02 mJ as compared to 0.30 mJ for methane.

Timeline chronology of hydrogen discovery, recognition and usage is shown in Figure 1.

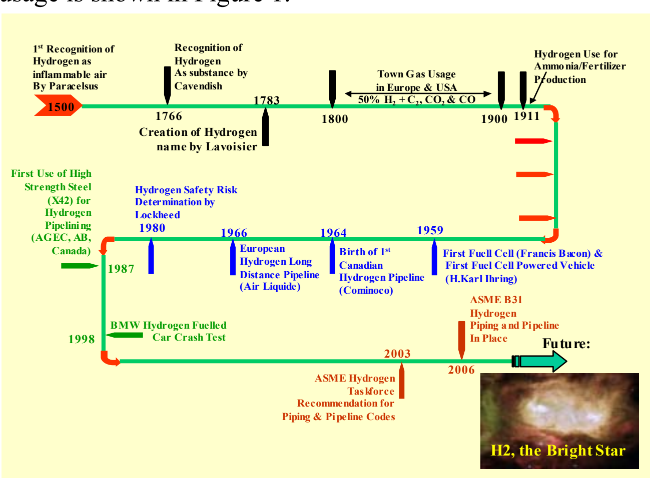

Figure 1 – Hydrogen and Hydrogen Pipeline Timeline

HYDROGEN PRODUCTION/USE.

Hydrogen is available as free element in various energy sources such as coal, natural gas, wind and hydropower etc. It is also available in secondary and chemical energy sources such as hydrocarbons, coke, refinery byproduct gases or synthetic, and biomass gas. Hydrogen is produced in several ways including:

- By the action of steam on heated carbon
- By decomposition of certain hydrocarbons with heat
- By the electrolysis of water
- By displacement from acids by certain metals
- By the action of sodium or potassium hydroxide on aluminum

In North America, hydrogen that is used in refinery processes is produced either by catalytic reforming of gasoline fractions or by steam reforming (SMR) of natural gas. Hydrogen is also produced by delayed or fluid coking in oil sands processing and by partial oxidation of residual oil. Figure 2 represent sources of and methods for production of hydrogen (Dears 2003).

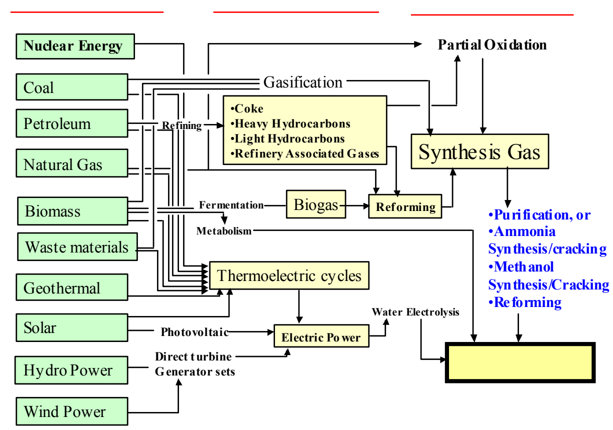

Figure 2: Summary of Hydrogen Sources and Production Techniques (Dears 2003)

Large quantities of hydrogen are required commercially for ammonia production and for the hydrogenation of fat and oils. It is used in large quantities to convert low grade crude oils into transport fuels like in methanol production, in hydro-de-alkylation, hydro-cracking (for heavy oil production), hydro-treating, and hydro-desulphurization. It is used as rocket fuel, as an alternative fuel to hydrocarbons for aviation and other uses (Reynolds and Slage 1974), for welding, for production of hydrochloric acid and for the reduction of metallic ores. It is used as an energy source for power generation and transportation. Ammonia and urea production consume more hydrogen than any other applications. The first time use of hydrogen for such productions was in 1911.

World consumption of hydrogen is 50 million tones per year and is growing at the rate of 10% per annum (IAEA, 2003)

ACCEPTANCE OF HYDROGEN AS FUEL

Figure 3 (James McKnight, 1998) represents a 200-year snapshot of the market share of major fuel types.

Included in this 200 year window is a projection approximately 60 years into the future to 2060. By viewing such a long period of time the major changes that have taken place in energy use, and those that are expected to take place, are very evident. The petroleum fuels that are so common today did not have a market share at all in 1860. It is also evident that while some appear on the graph as being in various levels of decline by 2060, other commercial sources such hydrogen will likely become dominant and accepted between 2015-2020. With this trend one may confirm the US Vision for Transmission to Hydrogen Economy by 2030, see Figure 4 (US DOE 2002).

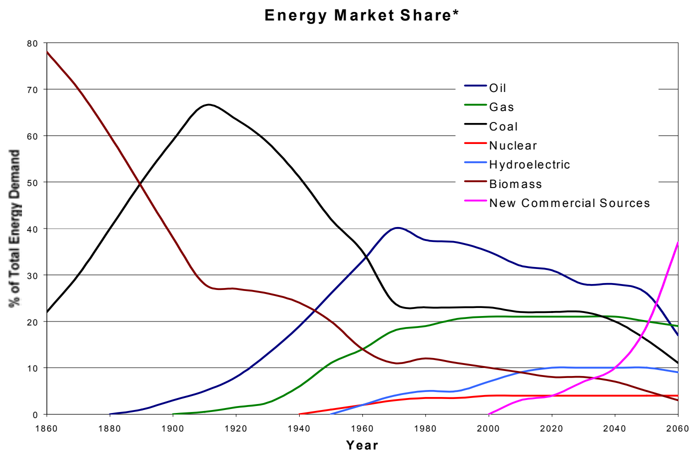

Figure 3: Energy Market Share, 1860 – 2060

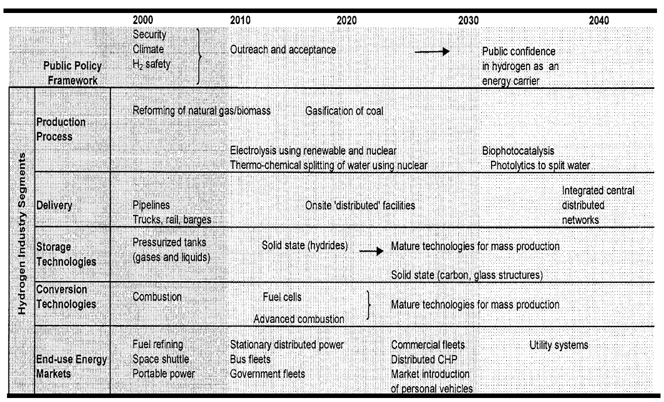

Figure 4 – Future for US Hydrogen Economy (US DOE2002)

HYDROGEN PROPERTIES IMPORTANT TO STORAGE & TRANSPORTAION

In order to understands issues related to the storage and transmission and hence the distribution of hydrogen, its properties need to be compared with other forms of common energy, Table 1. (L'Air Liquide 1976 & Nejat 2003).

Review of Table1 shows that hydrogen despite of a common negative perception on its safety, is an ideal fuel source and can be transported safely.

To transport equal amount of energy, the volume of hydrogen transported will be three times more than natural gas. However as hydrogen density is lower than natural gas, its comparative volumetric efficiency is higher. Detonation required to ignite hydrogen is a fraction of that required to detonate natural gas or gasoline. Very little is required to detonate hydrogen, and therefore explosive force is much lower. A hydrogen flame burns quickly and emits very little

Characteristics	Hydrogen	Natural Gas	Gasoline	Propane
Lower Hearting Value, (KJ/g)	120	50	44.5	46.1
Higher Heating Value, (KJ/g)	142	55.6		50
Self ignition temperature (°C)	585	540	228 - 501	470
Flame Temperature (oC)	2045	1875	2197	1980
Ignition/Flammability limit air (Vol%)	4.0 - 75	5.3 - 15	1.4 - 7.6	2.2 - 9.5
Minimum ignition Energy in air(μJ)	20	290	240	
Detonation limit in air (Vol%)	18 - 59	6.3 - 13.5	1.1 - 3.3	
Theoretical explosive energy (Kg TNT/m^3 gas)	2.02	7.03	44.22	
Diffision coefficient in air (cm^2/s)	0.61	0.16	0.05	0.11
Density @ NTP Kg/M3	0.0887	0.707	760-823 (4.4*)	582
Phase Condition	Gas	Gas	Liquid	Liquid
Toxicity to Humans	Non-toxic Simple Asphyxiant	Non-toxic Simple Asphyxiant	Poisonous, irritant to Lungs, stomach & skin	Non-toxic Simple Asphyxiant
Flame Emissivity %	17-25	25-33	34-43	

Note: * Indicate gaseous condition

Table 1: Properties of Hydrogen and Some Common Fuel.

heat (10% in comparison to hydrocarbons). This means that a hydrogen explosion and fire will do less damage to the immediate surrounding than natural gas or gasoline fire, while consequently creating less damaging gases caused by the burning of secondary material.

It is almost impossible to detonate hydrogen gas in open air making it a very safe fuel compared to other alternatives, (Kruse B et al. 2002). Hydrogen is 14.4 times lighter than air and rises at a speed of 20 m/s. Ventilation and other security systems are therefore necessary in enclosed spaces where hydrogen gas exists (Mohitpour et. al. 1988).

MODES OF STORAGE & TRANSPORTATION

To develop an economical and effective hydrogen systems, Improved methods for safe storage and transportation are required. The following addresses present methods and further research/improvement needs.

Storage

There are basically three options available to store large volumes of hydrogen or for fuel in transportation systems (Kruse 2002):

- Compressed hydrogen gas in a pressure vessel/pipelines
- Liquid hydrogen stored in insulated tanks and cryogenic dewers
- Hydrogen stored in a solid compound (metal and ceramic hydrides)

Transportation

Hydrogen can be transported using the following manner:

- Liquid Hydrogen Tankers – could be Hydrogen Rechargers / Liquid Hydrogen pumpers (the tankers could be adapted for rail, ocean or air)
- Compressed Gas Trailers (could be adapted for rail)
- Pipelines

The design, construction, operations and maintenance are governed by many codes and standards and are described elsewhere (NASA, 1997. Report NSS 1740.16 Chapter 8 and Appendix D).

There are advantages and disadvantages when utilizing the different transportation modes. Use of trailers / tankers provides more flexibility and can be used to deliver hydrogen to many locations. Larger amounts of hydrogen may be transported in liquid state. However additional precautions need to be taken when transporting hydrogen in liquid forms. The tankers / trailers need to be maintained, tested and remanufactured regularly inspected for to the wear and tear of transportation. The GH_2 trailers are generally of lower cost when compared to LH_2 tankers.

Pipelines systems, generally are expensive to construct particularly for liquid hydrogen (LH_2) transportation and also can be difficult if not impractical to maintain and operate as cross country transmission lines. LH_2 pipelines are often limited to short distance inter-plant systems. A combination of short distance LH_2 pipelines, high-pressure hydrogen gas (GH_2) transmission pipeline and GH_2 tube trailers, and local distribution mains may be used with increased flexibility and safety. To develop an effective hydrogen economy, all of the above modes of transportation are needed individually or in combination . For unique needs, requirements, lifecycle costs, and field conditions (regulations) need to be considered

For example a study was performed at NASA KSC to determine the best method to supply 4200 to 4500 psi pad batteries at the Shuttle Pads. The hydrogen is then transported through a piping system to purge shuttle onboard fuel cells. Presently two aged rechargers are used to deliver hydrogen to the pad batteries. The customer required that there were to be no piping configuration changes in the pad, and also rotating equipment could not be installed in vicinity of the pads (Tierney and Sharpe 2003).
The following options were considered:

- Fixed Recharger with a six mile pipeline
- Fixed compressor with six mile pipeline
- Mobile LH_2 Recharger
- Mobile GH_2 Compressor

The procurement of a new Recharger was recommended due to cost and versatility. The Recharger may be used for future hydrogen research plans.

PIPELINE TRANSMISSION OF GASEOUS HYDROGEN.

World pipeline experience

Although produced in large volumes as a by-product, very little of such hydrogen is recovered. Compression facilities are not usually available at these sources. The bulk of the hydrogen produced globally is consumed at or within pipeline distance of the production location. However world experience of hydrogen pipeline transmission is increasing because of increasing hydrogen consumption currently 50 million pounds daily in the USA alone. World hydrogen pipeline transmission experience is summarized in Table 2, which is an update that previously compiled by Mohitpour et. al (1990 & 2003).

High-pressure hydrogen pipeline transmission

The Transportation capacity of a given pipeline configuration to carry energy is lower when it carries hydrogen than when it carries natural gas. In a pipeline of a given size and pressure, while hydrogen will flow three times faster, it contains three times less energy per cubic meter and therefore only a comparative amount (1/3) of energy can be delivered. Since compressors operate on volume rather than energy content, considerably higher compression horsepower will be required.

Long distance pipeline transportation of hydrogen is currently limited to about 5500 kPa (800 PSI) Table 2. For large quantities of hydrogen requirements, transmission pipelines may be of large diameter and operate at higher pressures compared to natural gas pipelines. Moreover, these pipelines may have to be constructed from high strength steel line pipe (> X80). However, from a review of potential hydrogen uses, and demand over the next decade, (Mintz., et al 2002) it can be seen that hydrogen supply, transmission and distribution pipeline infrastructure is the most viable solution. From Mintz review and by taking advantage of the analysis of Bossel et.al (Bossel et.al 2002) who questioned the long term viability of hydrogen transmission by pipelines, one can design a practical hydrogen transmission system that potentially meets the near and intermediate term demands for hydrogen. Typical of such paths are shown schematically in Figure 5 illustrating a viable combinations of cross country and distribution pipelines, over the road transportation vehicles and local storage and compressors

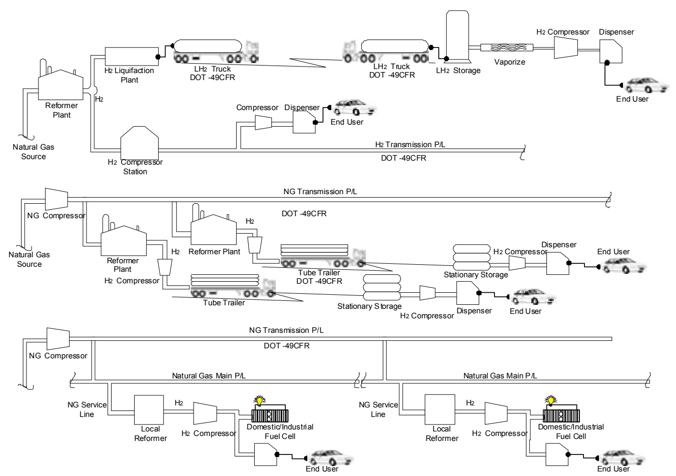

Figure 5 - Possible High Pressure Hydrogen Pipeline Transmission Path

Design Considerations

The supply infrastructure Figure 5 is a typical of what needs to be in place for transportation of large quantities of hydrogen gas. This infrastructure provides a continuous supply of hydrogen at reasonably manageable pressures. Local compressors can provide hydrogen at higher pressures depending upon the end user. For example an automobile refill station may need a compressor to fill automobiles to 34400 kPa (5000 PSI) pressure. In illustrated system transmission pipelines can operate at pressures up to 15500 kPa (2220 PSI) which is limited of ANSI AMSI 900# flange rating and with relatively smaller diameter pipe 273 to 356 mm (10 to 14 inches) for mainlines. Natural gas pipeline currently operate up these pressures. However, within the hydrogen economy regime, the pipeline operational requirements (e.g. pressures exceeding 20000 kPa (3000 PSI)) are likely to be more severe than those the pipeline industry is used to in natural gas transmission.

Location	Pipeline Material	Years of Operation	Diameter (mm)	Length (km)	Pressure (kPa) and Gas Purity (%)	Experience Reported	Status
AGEC, Alberta, Canada	Gr. 290 (5LX X42)	Since 1987	273 x 4.8 WT	3.7	3.790 kPA – 99.9	No	Operational
American Air Liquide Texas/Louisina, USA	API 5LX42, X52, X60 and others	?	3" to 14"	390	5100 kPa (740 PSI)	Yes	Operational
Air Products, Houston area, USA		Since 1969	114.3 – 324	100	345 – 5.516 (Pure H2)	No	Operational
Air Products, Louisiana	ASTM 106	1999 ?	101.6 – 304.8	48.3	3.447	Yes	Operational
Air Products, Sarnia (Dow to Dome plant)				3 app.		No	Operational
Air Products, Texas	Conv. natural gas line (steel)	>10	114.3	8	5,500 – Pure H2	Yes	Operational
Air Products, Texas	Steel, schedule 40	>8	219.0	19	1.400 – Pure H2	Yes	Operational
Air products, Nether land				45 Km	(throughput= 50 tons/day)		Operational
Chemische Werke Huis AG- Marl., Germany	Seamless equipment to SAE 1016 Steel	Since 1938	168.3 – 273	215	to 2,500: raw gas (throughput = 300 x 106 m^3)	Yes	Operational
Cominco B.C., Canada	Carbon Steel (ASTM 210 seamless)	Since 1964	5 x 0.8125 WT	06	>30,000.62 to 100% pure H2	No	Standby
Gulf Petroleum Cnd, (Petromont- Varnnes)	Carbon Steel, seamless, Sch. 40	--	168.3	16	93.5% H2; 7.5% methane	No	Operational
Hawkeye Chemical, Iowa	ASTM A53 Gr. B	3	152.4	3.2	2.757.6	Yes	Operational
ICI Billingham, UK	Carbon Steel	-	-	15	30,000 kPa, pure	No	-
L'Air Liquide, France, Netherland, Belgium	Carbon Steel, seamless,	Since 1966	sizes up to 12"	879	6,484 – 10,000 kPa; pure and raw	No	Operational
LASL, N.M.	ASME A357-Gr.5	-	25.4	6.4	13,788	Yes	Abandoned
Los Alamos, N.M.	5 Cr. – Mo (ASME A357 Gr. 5)	>8	30	6	13.790 pure	Yes	Abandoned
Linde, Germany	-	-	-	1.6 – 3.2	-	-	-
NASA-KSC, Fla	316 SS (austinitic)	>16	50	1.6-2	42,000 kPa	No	Operational
NSA-MSFC, Ala	ASTM A106-B	-	76.2	0.091	34470	Yes	Abandoned
Phillips Petroleum	ASTM A524	4	203.2	20.9	12,133-12,822	Yes	Operational
Praxair, Golf Coast, Tx, Indiana, California, Alabama, Louisiana, Michigan	Carbon Steel			450 Km	Commercial Purity H2 (500 MSCFD)		Operational
Rockwell International S.	SS-116	>10	250	-	>100,000 kPa; ultra pure	No	-
South Africa				80			?

TABLE 2: WORLD HYDROGEN PIPELINE EXDPERIENCE (MOHITPOUR ET AL, 1990 & 2003)

The primary consideration in a hydrogen system is the level of safety required to ensure public confidence and acceptance. Public acceptance of current failure rates in the natural gas pipeline systems cannot be the basis or extended to hydrogen systems. Compared to natural gas pipelines, hydrogen pipelines have admirable safety records (Chatterjee, 2002). However because of the negative perception of hydrogen safety ,the public will demand lower failure rates possible and ensure that stringent requirements in Codes and Standards and government regulations are in place.

Codes and Standards

There are a number of codes and standards that the industry in general follows for the design, construction and operation of hydrogen systems (Mohitpour, et.al. 2003). However these lack guidance for material selection and design for hydrogen compatible systems particularly high-pressure transmission pipelines.

Following the work of various ASME task groups under the DOE directive (US DOE 2002), the ASME Board on Pressure Technology Codes and Standards (ASME- BPTCS) has initiated the development of an independent consensus standard/code, B31.H_2 for hydrogen piping and pipelines, (ASME 2003). The B31.H_2 piping and pipeline standard/code will be based on the various current ASME Boiler, and other applicable codes. It may be remarked that any suggested choice of material in the Codes and Standards need to be based on a thorough understanding of its properties in hydrogen environment. Materials Science and Engineering research is important to be performed in this aspect to provide necessary confidence level to the users of the Codes and Standards as well as public.

PIPELINE MATERIALS SELECTION/DESIGN

As shown on Table 2, historically carbon or stainless steel pipelines were used to transport hydrogen. Because of the unique physical and chemical properties of hydrogen, an extensive understanding of the effect of hydrogen on materials is necessary for safe use. Selections of materials for hydrogen service require an understanding of how hydrogen embrittlement is manifested, Figure 6.

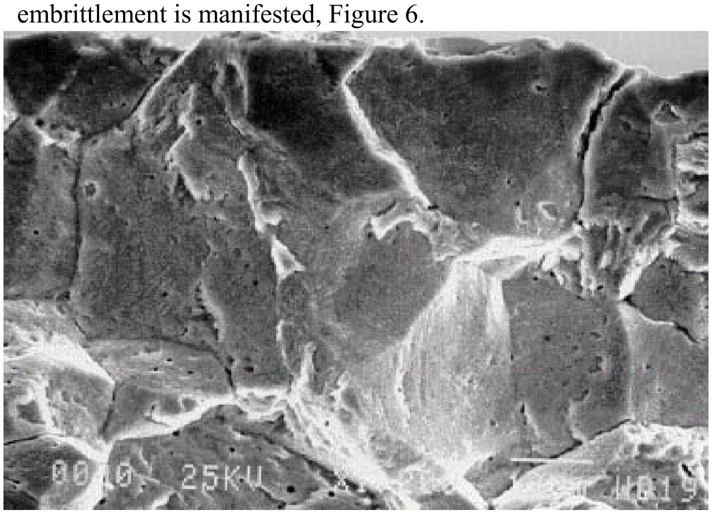

Figure 6 – Electron Microscopic Characteristic of Hydrogen Embrittlement (NASA 1997).

Embrittlement causes a significant deterioration in the mechanical properties of metals. There are three forms of basic embrittlement (NASA 1997). There are:

- Environmental hydrogen embrittlement that has been observed in metals and alloys plastically deformed in a gaseous hydrogen environment. This results in increases in surface cracks, ductility loss and fracture stress reduction. Cracks start at the surface.
- Internal hydrogen embrittlement caused by absorbed hydrogen. Small amounts of hydrogen may cause premature failures in some metals; the failures may occur with little or no warning, as these cracks start internally.
- Hydrogen reaction embrittlement that occurs when the absorbed hydrogen combines with one or more of the constituents of the metal to form a brittle hydride. This reaction occurs more readily at elevated temperatures. Hydrogen assisted cracks are usually weldments, and heat affected zones.

Technical report NSS 1740.16 Table A5.7 (NASA 1997), is an excellent source for testing methods and locating cracks for each embrittlement type.

Materials with as body centered cubic (BCC) structure (such as iron, low alloy steels, chromium, molybdenum, niobium, and zinc) are more susceptible to hydrogen permeation than those with face centered cubic (FCC) materials (austenitic stainless steels, aluminum alloys, copper and copper alloys). The yield and tensile strength of BCC structure depend to a great extent on the temperature, and therefore exhibit a substantial loss of ductility within a narrow temperature range.

Extensive research and experience due to the use of hydrogen has been developed. Table 3 summarizes material compatibility for hydrogen service (NASA 1997), which includes those for piping as well as pipeline applications. Review of the Table 3 indicates that gray, ductile or cast iron, nickel steels is not suitable for any hydrogen service. Austenitic stainless steels, aluminum (including alloys), copper (including alloys), and titanium (including alloys) are generally acceptable for most hydrogen service applications. Carbon steels, and high strength low alloy (HSLA) steels are used for gaseous hydrogen service that are not susceptible to hydrogen attack at low prssures. Research also indicates that high strength steels (above 100 ksi), are more susceptible to hydrogen embrittlement, and the use of thicker low strength steel is recommended for pipelines (Mohitpour et. al. 1998, 1990). However, there are many issues to be considered when selecting materials for hydrogen service, such as cost, availability, durability, and application severity so that appropriate material can be selected. Research is nonetheless needed to determine operating conditions of when it is safe to use each material.

Steels for Hydrogen Service at elevated temperatures are referred to in API Recommended Practice RP 941 (1997). The document shows graphs with temperature and pressure axis showing satisfactory areas for using carbon steel, and various Cr-Mo steels.

Material	Service			Remarks
	GH_2	LH_2	SH_2	
Austenitic stainless steels with >7% nickel	Yes	Yes	Yes	Some make martensitic conversion if stressed above yield point at low temperature
Type 304				May be used for piping, valves, plates, forging & fittings Minimum temperature = -425 °F
Type 304L				May be used for piping, and plates Minimum temperature = -425 °F
Type 310				May be used for plates, forging & fittings Minimum temperature = -325 °F
Type 316				May be used for piping, valves, plates, forging & fittings Minimum temperature = -425 °F Least resistant to embrittlement for 10000psi gas at 72 °F
Type 321				May be used for piping, plates, forging & fittings Minimum temperature = -325 °F
Type 347				May be used for piping, plates, forging & fittings Minimum temperature = -425 °F Prone to crack during welding, proper welding precautions need to be taken prior to welding.
Aluminum & alloys: WP1100-0, B361; 1100-0, B241, 3003-0, B241; 5083-0, B241; WP6061-T6, B361; 6061-T6, B241.	Yes	Yes	Yes	Minimum temperature = -452 °F Different aluminum alloys may be used for all types of equipment Stress allowable is much lower than stainless steel
Carbon Steels: A285 Grade C, A584; and A442 Grade 50, A672	Yes	No	No	Becomes brittle for cryogenic use. Minimum temperature = -20 °F
Copper and its alloys (such as brass, bronze, and copper-nickel): Cu, B283, B152, & B42 annealed; Red brass pipe, 90Cu-10Ni, B171 & B466; 70Cu-30Ni, B171 & B466	Yes	Yes	Yes	Minimum temperature = -452 °F Different copper alloys may be used for all types of equipment Stress allowable is much lower than stainless steel
Gray, ductile, or cast iron	No	No	No	Not to be used for hydrogen service
Low alloy steels	Yes	No	No	Too brittle for cryogenic use
Nickel and its alloys (such as Inconel & Monel): Ni, B366, B161 & B162; Ni-Cu, B564, B127, & B165; Ni-Cr-Fe, B564, B168 & B167.	No	Yes	Yes	Susceptible to hydrogen embrittlement Minimum temperature = -325 °F Different nickel alloys may be used for all types of equipment
Nickel Steels (such as 2.25, 3.5, 5 and 9% Ni)	No	No	No	Looses ductility at cryogenic temperatures. Can be used for cryogenics (9%, -323 °F; 5% - -260 °F; and 3.5%, -150 °F)
Titanium and its alloys: Ti, B337; and Ti-0.2Pd, B337.	Yes	Yes	Yes	Minimum temperature = -75 °F
Asbestos impregnated with teflon	Yes	Yes	Yes	Avoid use because of carcinogenic hazard
Chloroprene rubber (Neoprene)	Yes	No	No	Too brittle for cryogenic use
Dacron	Yes	No	No	Too brittle for cryogenic use
Fluorocarbon	Yes	No	No	Too brittle for cryogenic use
Mylar	Yes	No	No	Too brittle for cryogenic use
Nitrile (Buna-N)	Yes	No	No	Too brittle for cryogenic use
Polyamides (Nylon)	Yes	No	No	Too brittle for cryogenic use
Polychlorotrifluoroethylene (Kel F)	Yes	Yes	Yes	Recommended for o-rings and gaskets, for cryogenic use.
Polytetrefluoroethylene (Teflon)	Yes	Yes	Yes	Recommended for o-rings and gaskets, for cryogenic use.

Table 3 - Summary of material compatibility for hydrogen service (NASA 1997)

The effect and level of hydrogen embrittlement on materials is dependent on a large number of variables such as:

- Environment temperature and pressure
- Hydrogen purity and concentration
- Hydrogen exposure time
- Stress state, secondary stresses, temperature range etc.
- Metal microstructure, physical, mechanical properties
- Metal surface finish and conditions
- Type of material crack front

Tests to determine the effect of pressure on three high strength steels (A533-B, 1022 High Mn Carbon steel, and 250 Maraging steel), show that the material becomes more brittle as hydrogen pressure is increased (. Thompson 2002). It is concludes that the allowable stress is a function of pressure for materials used for hydrogen service. NASA (1997) in their report NSS1740.16 also conclude that many carbon steels become more susceptible to embrittlement with the increase of pressure.

Hydrogen reaction embrittlement also increases at elevated temperatures. The hydrogen combines with the carbides in steel forming methane or oxides in copper forming steam. Mechanical creep (deformation under sustained load) is accelerated resulting in quicker material failure, (Thompson, 2002).

Line Pipe Materials in Hydrogen Service.

Historically, line pipe materials selection followed the list of specifications in Appendix A to 49 CFR Part 192 such as the API 5L (API 2000). API standard 5L is used extensively worldwide with proven safety record in natural gas service. The design basis is stipulated in the regulations, and industry codes such as the ASME B31.8 "Gas Transmission and Distribution Piping Systems". The design pressure is governed by the specified minimum yield strength (SMYS) of the steel. The designer must consider other factors such as allowable design factors, corrosion allowance, seismic loads and possibility of environmental effects as applicable.

With the demand for natural gas increasing year by year, to economically justify high pressure long distance transmission, the industry initiated the use of API grade X-70 (580 Mpa-70 Ksi) and X-80 (550 MPa -80 Ksi) line pipe. Higher-grade steels allow higher operating pressures or larger diameter yet limiting the wall thickness so is the current practices of production, welding, and construction. Currently the industry is testing the use of API X-100 material.

One of the major considerations in the design of high-pressure natural gas pipelines is the prevention of long running fractures by selecting line pipe with adequate fracture toughness. It was the publication of the 42nd edition of API 5L standard in 2000 that provided for specific supplemental requirements for toughness (PSL-1) and mandatory toughness requirement (PSL-2) for line pipe steel. With mandatory toughness requirement, pipelines have proven to be safer operationally. It is important to note however, codes and standards, federal safety regulations, or other industry standards or the line pipe manufacturers have not provided for any specific requirements as related to line pipe for hydrogen service. This issue is critical when it is contemplated to use higher-grade steels with yield strengths greater than 482 Mpa (80Ksi), with relatively complex chemistry necessitated for improved resistance to corrosion and fracture for hydrogen service. Steel line pipe with yield strength of 685 MPa (100 Ksi) or greater, are made with special production method including micro-alloying thermo-mechanical rolling control. Almost all of the modern high strength steels tend to have a high yield to ultimate strength ratios (Smith 2003). While the research associated with the development of these high-grade steels would indicate that the material is suitable for natural gas, their use in hydrogen service has not been addressed, and substantial research is needed to incorporate theses specifications into any of the hydrogen codes and standards.

Joint Design

Welding is the preferred joint for hydrogen pipelines. In some steels, especially those with a high alloy content, the heat-affected zone produces hard spots, residual stresses, and a microstructure conducive to embrittlement. To reduce this effect post weld annealing, / heat treatment is required. For pipelines it is important to select a material where the welds can be easily made in the field and also requires minimum heat treatment. While it is a normal practice to qualify weld procedures by determining the adequacy of mechanical properties, ductility and toughness (ASME Section IX and API RP 1104), no testing is stipulated for determining the material compatibility with aggressive products such as hydrogen.

Approach to mitigate the effect of Hydrogen Embrittlement

To mitigate the effects of embrittlement on materials, the following need to be considered:

- Select materials for which sufficient performanced data and industry consensus for suitability in hydrogen service is available.
- Evaluate welding procedures used in manufacturing and field joints for fitness for service in hydrogen environment
- Avoid sources of stress concentration
- Proper surface finish
- Incorporate a thorough integrity management plan. Incorpaorate appropriate in service inspection method to discern hydrogen assisted cracking, and embrittlement
- Use hydrogen attack inhibitors

Performance Criteria

The following should be considered when choosing piping material for hydrogen systems:

- Hydrogen state (slush, liquid, or gas)
- Temperature, and/or temperature range
- Pressure
- Other secondary loading conditions
- Compatibility with operating environment (also include effects due to corrosion)

- Ease of fabrication and assembly
- Potential to minimize damage due to hydrogen fires.
- Cost

RESEARCH & DEVELOPMENT

The interfacing of hydrogen delivery systems, form production plants to local distribution facilities and finally to end users are a challenging aspect that must be addressed by research and development efforts. Coordinated research efforts is necessary to understand how line pipe steels are affected when exposed to hydrogen (particularly at high pressures), how to prevent or minimize the failure probability of a system, and finally to gather critical data that is essential for the development of codes and standards and government regulations.

Areas that may be pertinent to short term and near term goals set for the hydrogen economy:

Conversion of Existing Natural Gas Pipelines

The failure rates related to the existing natural gas pipelines may not be acceptable for hydrogen service. Each segment identified for conversion must be evaluated the entire length of the segment to determine its condition, previous failure history, and the steel compatibility for hydrogen service. Additionally, weld qualification procedures, mill test data and additional testing of samples taken at various locations of the segment will add to the confidence for safe operation. Pipelines of X-65 grade or higher may require fracture mechanics type testing and analysis.

Alternative Line Pipe Material

TransCanada Pipeline Inc., has field-tested a 25 Km 915-mile) 48-inch diameter Composite Reinforced Line Pipe (CRLP™) in the last two years. (Zimmerman et. al 2002 and Harrison 2003).

From the original concept and pipe segments produced by Norm Fawley, of NCF Industries, TransCanada designed and installed the pipe segment in their Saratoga section of the Western Alberta natural gas system Figure 7.

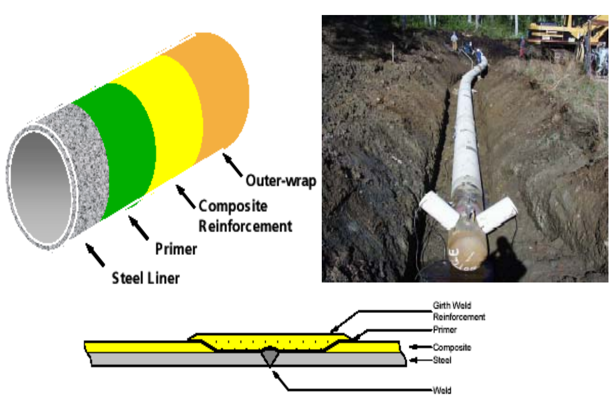

Figure 7: Experimental Composite Reinforced Line Pipe and Weld Joint (Zimmerman et. al. 2002).

The design has the advantage that high strength composite filament wound on a thin wall line pipe provides a pressure carrying capability much greater than an all steel pipeline. The Composite materials similar to the one used in TransCanada project, has been proven in other applications to have adequate long-term durability and strength retention. Therefore it appears that a CRLP type pipeline can be engineered to limit liner stress at a level deemed to be safe in gaseous hydrogen environment, and for high operating pressures it is a viable alternative to use modern higher strength (X-100 and X-120) steel line pipe. However there are issues such as the optimum high wall stress that the steel liner need to be to make use of composite strength efficiently, definition of minimum strength levels for composites, production quality control, maintenance and in-service inspection technologies. When considering CRLP for high-pressure hydrogen service, as either a storage vessel, or a hydrogen transmission pipeline many issues require attention. DeWolf et.al (1999). These include understanding of welded liner fatigue, girth weld integrity, crack initiation and propagation once a full penetration crack is formed in the liner, and the full scale demonstration burst tests with hydrogen as the medium (Leighty 2003).

Material Performance Criteria

Hydrogen pipelines must provide a safety level an order of magnitude higher that current experience with natural gas pipeline. For a relatively faster implementation of hydrogen economy, transmission and distribution pipelines are likely the key, provided adequate steps are taken to select materials that provide maximum safety, practical to use for large infrastructure, and economical. To an extent, the line pipe materials (API X-52, to X80 grade pipe) currently used in natural gas service may meet the short-term needs. Towards this goal the line pipe steel, either used for a (conventional) all metal pipeline, or as liner in a fiber-wound- polymer composite pipeline, must primarily have a high degree of resistance to degradation in high-pressure hydrogen environment.

Design Considerations

In order to meet certain energy supply demand a practical solution is to choose large diameter, higher design pressure pipeline. A high design maximum allowable pressure may likely induce the designer to use high strength steel resulting in thinner wall pipe. Such pipelines require special attention over and above a similar pipe in natural gas service. For example, a third party damage resulting in dent and gouge of certain severity may be of equal potential for in-service failures in either natural gas or hydrogen service. The consequences of hydrogen pipeline can be much more serious, and as such to create public acceptance of hydrogen pipelines, an understanding of the effect of various parameters on pipeline integrity throughout its design service life is an essential research topic.

There are number factors that need consideration in determining the suitability of a material for hydrogen service:

- Minimum Specified Yield Strength
- Minimum Specified Tensile Strength
- Yield Strength to tensile Strength Ratio
- Steel Chemistry
- Weld-ability

- Minimum Design Temperature
- Fracture Initiation Toughness
- Corrosion resistance, and corrosion prevention
- Failure prevention program including periodic inspection
- Resistance to environmentally caused degradation

There is a need to develop allowables and limitations of the pipeline material parameters from the existing data and/or further research and testing so that meaningful information is available for codes and standards, and to those who develop regulations. For example, it is known that many low strength and HSLA steels, typical of older line pipe steels, are susceptible to some form of hydrogen induced effect resulting in considerable degradation of properties such as notch tensile strength, brittle-ductile transition temperature and toughness Such an effect will change basic design considerations resulting in pipelines operating at higher stresses thus causing other mechanical and hydrogen related problems (Louthan 1982, Troina, 1960). Research is needed to understand if the newer steels with improved chemistry, and manufacturing process controls are better so that pipelines with higher stresses can be operated safely.

Hydrogen Environment Considerations:

Hydrogen Embrittlement: Available research based information indicates that steels exposed to hydrogen environment might reduce mechanical strength and fracture properties. The phenomenon " hydrogen embrittlement" can be potential problem with typical pipelines and in pipeline operating conditions. There are many theories to explain hydrogen embrittlement process. The pressure theory intended to explain embrittlement in dry hydrogen environment describes that the embrittlement process consists of atomic hydrogen diffusing into metal from hot or highly stressed surfaces and combining to form either hydrogen molecule (molar hydrogen) to react with carbon in the metal to form methane gas in small voids along the grain boundaries. As the gas undergoes volume change, local stresses fluctuate to initiate micro-cracks. In the absence of corrosive environment, the micro cracking progress over time will result in loss of ductility, and toughness. Structural failures resulting from hydrogen induced cracking occur suddenly in a brittle manner. It has been shown (Loginow and Phelps, 1974) that under sustained load, hydrogen degradation can be characterized by threshold stress intensity K_H typical for various type steels. Lower K_H would result in smaller defect size or lower operating pressures. It is not clear, however if this phenomenon varies with the pressure, microstructure and chemistry of steel and increasing pressure. If such a phenomenon can occur in pipelines operating in high pressure in hydrogen service, it is important to be cautious in the choice of materials for which K_H is unknown. In sustained high-pressure hydrogen environment and with relatively modern high strength steels, any concern is justified because there appears to be no data available for pipeline steels to judge severity of hydrogen. More importantly, a research program is needed for the choice of existing line pipe materials.

Crack Growth in Hydrogen Environment:

Crack growth process in metals is governed by mechanical driving force at the crack tip , which is characterized by stress intensity K. The process is stepwise stable growth under sustained loading as well as under cyclical loading. If the environment is hydrogen, the process includes transport of dissociated hydrogen into to the lattice structure ahead of the crack tip causing enhanced crack growth in any of the above crack growth processes. Combination of hydrogen enhanced crack growth and embrittlement is the phenomenon that needs utmost attention by the researchers.

Fatigue Crack growth in Hydrogen Environment:

The conventional method of fatigue analysis is based on prediction of cyclic life based on applied stress or strain range vs. cycles to failure S-N curves. These curves are developed for each material by testing smooth round bar specimens subjected to full reversal loading. Consequently, the life includes crack initiation and crack propagation. Given the premise that materials do have or generate in service, cracks or crack-like defects, fracture mechanics approach is warranted (Broek, 1983). Fatigue as function of crack growth per cycle and stress intensity range at the crack tip and is expressed in the form:

$$da/dn = C(\Delta K)^n$$

where C and n are the experimental values that define the fatigue behavior of the material.

Published fatigue data for pipelines that can be used as a base line to determine the effect of hydrogen environment are scarce. There is limited data on high strength quenched and tempered steel cylinders in hydrogen service, (Kisten and Runow 1981), Figure 8. From Figure 8, it cab be observed that for the Q&T steels, in hydrogen environment an order of magnitude loss in cyclic life is possible. There is a need to obtain basic fatigue data in air environment and in hydrogen environment. The experimental data need to include fatigue threshold, stable fatigue crack growth and low cycle fatigue that can be helpful to develop fatigue design curves for various pipeline steels.

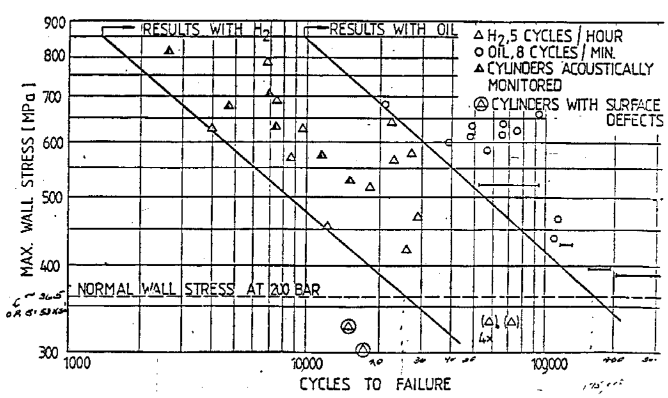

Figure 8. Fatigue Data for Pipeline Material (Kisten and Runow 1981).

Weldability and Weld qualification procedures:

The issue of weldability of high strength steels should include weld quality. Since flawless production welds are but a myth to consider, there is a need to develop defect acceptance criteria for hydrogen environment much the same as natural gas service. Weldability and fracture tests should be a critical research issue to codes and standards development

NEW PIPING

Existing Materials

Determine acceptable materials (from existing) for piping and also the following information:

- Material constraints (pressure and temperature)
- Required surface finish
- Method for forming material (grain size)
- Surface finish
- Coating requirements
- Fabrication requirements

Reference may be made to API Recommended Practice 934. A similar document should be prepared for each recommended material to ensure material quality and safety.

For each acceptable material determine the allowable stresses for each material at the different pressures and temperatures. To determine the material effects due to hydrogen induced embrittlement and cracking use methods described in ASTM F519 and NACE Std. TM0284 respectively.

The susceptibility of metals to the hydrogen attack depends upon several variables. Metal composition is more important variables. The strength fracture toughness, and weldability of newer high strength pipeline steels is obtained by adding alloying elements such as nickel, titanium etc. While these elements improve mechanical properties, a trade of occurs with affecting corrosion resistance, and crack propagation toughness, and weldability. More importantly it is known to materials science researchers that hydrogen attack is likely in metals containing the alloying elements used in pipeline steels. It is recommended that a research program is needed to better understand micro-mechanics and metallurgical aspects of the newer high-strength pipeline steels.

Developing New Materials

An effort should be made to develop materials that are less prone to hydrogen embrittlement. Particular emphasis should be made to the factors mentioned above and in addition life cycle costs should be considered. When developing new materials, many ideas and previous research is referred to on A.W. Thompson – Materials for Hydrogen Service. This paper addresses manifestations of hydrogen damage, material characteristics, behavior of alloy systems, and structural behavior. Some of the highlights include the following:

- An idea to research into steel with Silicon and titanium instead of Carbon and Manganese with nickel and carbon contents balanced.
- Also stated "The other factor is grain size; both strength and toughness are increased by decreases in grain size, while both strength and toughness are increased by decreases in grain size; however resistance to hydrogen embrittlement is generally increased ".
- A discussion of age-hardening Stainless Steels and creating "stainless super-alloy".

Research should also be performed to develop any composite materials. Refer to NASA Tech Brief MFS – 31632.

CONCLUSION

In conclusion to improve the hydrogen economy new economical materials need to be developed for high pressure transportation of hydrogen by pipelines. To increase the safety and quality of hydrogen pipelines, a comprehensive performance code addressing design, construction, operation and maintenance of hydrogen systems needed to be developed.

The proposed combination of various modes of transportation (GH_2transmission/distribution pipelines, along with over the road tube trailer and LH_2 tankers) may be the final solution for economic and safe hydrogen supply.

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